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A NEW SEMICLASSICAL APPROACH TO THE MOLECULAR
DYNAMICS--LABEL VARIABLE CLASSICAL MECHANICS

Shenghua Shi

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A New Semiclassical Approach to the Molecular Dynamics--Label Variable

Classical Mechanics

Shenghua Shi

Department of Chemistry, and Materials and Molecular Research Division
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

Abstract

A new semiclassical approach to molecular collision dynamics is developed. In this approach the state of a system is described by a unit vector in Hilbert space. By choosing a reference unit vector and a continuous mapping a correspondence between the vector in Hilbert space and the point in a label space is established, i.e., the vector in Hilbert space is parameterized or labeled by complex variables. It is shown that the label variables formally obey classical mechanics. Thus, the time evolution of the vectors in Hilbert space, i.e., the evolution of the states of the system, can be determined by calculating the evolution of the label variables classically. To illustrate this idea, the formalism for calculating the vibrational transition probability in the collinear collision A + BC is presented, and a demonstrative calculation for the collinear Secrest-Johnson model of He + H_2 vibrationally inelastic scattering has been carried out. The comparison with the exact quantum results shows that the agreement is encouragingly good.

I. Introduction.

In quantum mechanics the state of a system corresponds to a unit vector in Hilbert space. The dynamics is governed by the Schrödinger equation which, in practical calculation, often leads to a prohibitively large number of coupled differential equations. In recent years many dynamical calculations have utilized classical and semiclassical methods. In classical mechanics the state of a system is specified by the coordinates and momenta of the particles in the system which evolve according to Hamilton's equations, which are easy to deal with, but classical mechanics is of course only an approximation to molecular dynamics. Semiclassical methods--e.g., multidimensional WKB methods like classical S-matrix theory,[1] and time-dependent wave-packet methods[2]-- are thus appealing since they combine the computational simplicity of classical mechanics with an approximate description of quantum effects.

In a series of papers on continuous representation theory by Klauder[3] an interesting semiclassical idea is presented. One begins with establishing a correspondence between vectors $|\Phi\rangle$ in Hilbert space $\mathcal{H}$ and sets of labels $\underset{\sim}{\ell}$ in an abstract label variable space L by a mapping $M(\underset{\sim}{\ell}): \underset{\sim}{\ell} \in L \rightarrow |\Phi[\underset{\sim}{\ell}]\rangle \in \mathcal{H}$. It has been shown[3] that within certain restriction the label variables formally follow the laws of classical mechanics, so that the evolution of the vector in Hilbert space, i.e., the state of the system as a function of the time, can be determined by calculating the time development of the label variables classically. In this paper we apply these ideas to the problem of molecular scattering and develop the formalism for calculating the transition probability of inelastic scattering as an alternative semiclassical approach to molecular dynamics.

In Section II, we demonstrate the basic idea of this approach by considering an elementary example of a single nonrelativistic particle free to move in only one dimension. The formalism for calculating the transition probability of vibrationally inelastic scattering in the case of A + BC collinear collision is derived in Section III, and an illustrative calculation for the Secrest-Johnson model system of He + H_2 collinear collision is presented in Section IV. As will be seen, the presented methodology, at least within the mode that it is applied here, has some features in common with earlier semiclassical wave packet approaches, but there are significant differences; Section V concludes with a discussion of this comparison.

II. Classical Mechanics of Label Variables--The Basic Idea.

The basic problem in quantum dynamics is to determine the evolution of the state vector in a Hilbert space. To this end, the present approach first establishes a correspondence between the state vector in the Hilbert space and label variables in a label space, and these label variables are found formally to obey the classical Hamilton equations of motion. One can then determine the time development of the state vector by solving classical equations of motion for the label variables by means of standard classical trajectory techniques. It is illustrative to consider first the case of a single, nonrelativistic particle free moving in only one dimension. Most of this section closely follows Klauder's[3] presentation.

First one chooses a unit vector $|\Phi_0\rangle$ in the Hilbert space $\mathcal{H}$ of the system as a reference vector. Thus,

$$\langle\Phi_0|\Phi_0\rangle = 1 \quad . \tag{1}$$

In principle the reference vector $|\Phi_0\rangle$ can be any proper vector in the Hilbert space. A pair of self-adjoint operators acting in the Hilbert space are denoted by $\hat{Q}$ and $\hat{P}$; for example, $\hat{Q}$ and $\hat{P}$ might be the position and momentum operator, respectively. These operators obey the canonical commutation relation

$$[\hat{Q},\hat{P}] = i\hbar \quad . \tag{2}$$

Using these operators one can generate a two-parameter, unitary family of operators

$$\hat{U}[p,q] \equiv e^{-iq\hat{P}/\hbar}\, e^{ip\hat{Q}/\hbar} \tag{3}$$

that satisfy the composition law

$$\hat{U}[p,q]\ \hat{U}[p',q'] = e^{ipq'/\hbar}\ \hat{U}[p+p',q+q'] \quad , \tag{4}$$

as well as the basic relation

$$\hat{U}^{-1}[p,q] = \hat{U}^{+}[p,q] = e^{-ip\hat{Q}/\hbar}\ e^{ip\hat{P}/\hbar}$$

$$= e^{ipq}\ \hat{U}[-p,-q] \quad . \tag{5}$$

Here p and q denote two arbitrary complex parameters. By acting on the reference vector $|\Phi_0\rangle$ with the unitary operator $\hat{U}[p,q]$ one defines the unit vector

$$|\Phi[p,q]\rangle \equiv \hat{U}[p,q]|\Phi_0\rangle \quad , \tag{6}$$

which is labeled by p and q. It can be shown[4] that the set of these vectors $|\Phi[p,q]\rangle$ for all p and q form a continuous basis G of the Hilbert space $\mathcal{K}$ in the sense that we can resolve the identity operator as

$$I = \int |\Phi[p,q]\rangle\ \frac{dp\ dq}{2\pi\hbar}\ \langle\Phi[p,q]| \quad ; \tag{7}$$

therefore, an arbitrary vector $|\psi\rangle \in \mathcal{K}$ can be expressed in terms of the set of these vectors

$$|\psi\rangle = \int |\Phi[p,q]\rangle\ \frac{dp\ dq}{2\pi\hbar}\ \psi(p,q) \quad , \tag{8}$$

where $\psi(p,q) \equiv \langle\Phi[p,q]|\psi\rangle$ is a representation of the vector $|\psi\rangle$ in this continuous basis G. Now if one imposes on the reference vector $|\Phi_0\rangle$ the restrictions

$$\langle\Phi_0|\hat{P}|\Phi_0\rangle = 0 \qquad\qquad\qquad (9a)$$

and

$$\langle\Phi_0|\hat{Q}|\Phi_0\rangle = 0 \qquad , \qquad\qquad (9b)$$

i.e., the mean values of $\hat{P}$ and $\hat{Q}$ in the reference state are zero, then it is easy to show that

$$\langle\Phi[p,q]|\hat{P}|\Phi[p,q]\rangle = p \qquad\qquad\qquad (10a)$$

and

$$\langle\Phi[p,q]|\hat{Q}|\Phi[p,q]\rangle = q \qquad . \qquad\qquad (10b)$$

This means that for such a choice of the reference vector the label variables p and q acquire a physical significance, i.e., p and q now are the mean values of the operator $\hat{P}$ and $\hat{Q}$ in state $|\Phi[p,q]\rangle$, respectively. Equations (9) and (10) immediately lead to the following canonical kinematical form

$$i\hbar\langle\Phi[p,q]|\dot{\Phi}[p,q]\rangle = \langle\Phi[p,q]|e^{-iqP/\hbar}[\dot{q}\hat{P}-\dot{p}\hat{Q}]e^{ip\hat{Q}/\hbar}|\Phi_0\rangle$$

$$= \langle\Phi_0|[\dot{q}(\hat{P}+p) - \dot{p}\hat{Q}]|\Phi_0\rangle$$

$$= p\dot{q} \qquad , \qquad\qquad (11)$$

where the dot denotes the time derivative.

Consider now the equation of motion for evolution of the label variables p and q. As well known in quantum mechanics[5] the time evolution of a state obeys the Schrödinger equation

$$i\hbar \frac{d|\psi>}{dt} = \hat{H}|\psi> \quad , \qquad (12)$$

where $\hat{H}$ is the Hamiltonian of the system. The solution of this equation can be formally written as

$$|\psi(t)> = e^{-i\hat{H}t/\hbar} |\psi(0)> \quad , \qquad (13)$$

if $\hat{H}$ does not depend on time t explicitly. The Schrödinger equation can be deduced from the extremization of the quantum action functional

$$I = \int [<\psi|i\hbar\dot{\psi}>-<\psi|\hat{H}|\psi>]dt \qquad (14)$$

under unrestricted variation of the vector $|\psi(t)>$. The unrestricted variation means that the vector $|\psi(t)>$ can be any vector in the whole Hilbert space $\mathcal{H}$. Among all the vectors in Hilbert space only the vector which causes the action functional I to have an extreme value will correspond to a real state of the system. Suppose now the variation of the vector $|\psi>$ is limited to a fairly restricted set of unit vectors such as the basis set vectors $|\Phi[p,q]>$ just defined. In other words, one uses $|\Phi[p,q]>$ instead of $|\psi>$ in the expression of the action functional in Eq. (14), and with the help of Eq. (11) one obtains

$$I' = \int dt \; \{i\hbar <\Phi[p,q]|\dot{\Phi}[p,q]> - <\Phi[p,q]|\hat{H}|\Phi[p,q]>\}$$

$$= \int dt \; (p\dot{q} - H) \qquad\qquad (15)$$

with

$$H \equiv <\Phi[p,q]|\hat{H}|\Phi[p,q]> \qquad . \qquad\qquad (16)$$

One immediately recognizes that formally this is a classical action functional. The extremal variation of I' with respect to arbitrary variation of p and q yields the classical Hamilton's equations of motion

$$\dot{q} = \partial H/\partial p = 0 \qquad\qquad (17a)$$

$$\dot{p} + \partial H/\partial q = 0 \qquad . \qquad\qquad (17b)$$

There are two reasons why we have used the word "formally" here. First, H(p,q) is not equal to the classical Hamiltonian $H_{cl}(p,q)$ which has the functional form of the quantum mechanical Hamiltonian with explicit p and q substitution for the operators $\hat{P}$ and $\hat{Q}$, respectively. There is an additional term $O(\hbar,\Phi_0,p,q)^3$,

$$H(p,q) \equiv <\Phi[p,q]|\hat{H}|\Phi[p,q]>$$

$$= <\Phi_0|\hat{H}(\hat{P}+p,\hat{Q}+q)|\Phi_0>$$

$$= H_{cl}(p,q) + O(\hbar,\Phi_0,p,q) \qquad . \qquad\qquad (18)$$

For nonpathological Hamiltonians O depends only on the positive powers of $\hbar$. Hence, in this case

$$\lim_{\hbar \to \infty} O(\hbar, \Phi_0, p, q) = 0 \quad .$$

That is, in the classical limit $\hbar \to 0$, one has $H(p,q) = H_{cl}(p,q)$ so that Eq. (17) becomes the conventional classical equation of motion. Since classical mechanics arises only in the formal sense, one can just as well adopt $H(p,q)$ itself as the "classical" Hamiltonian. Second, in classical mechanics p and q refer to the momentum and coordinate of a particle. Here, however, p and q just represent label variables for the state vector $\Phi[p,q]$. The physical significance of p and q depends on the choice of the reference vector $|\Phi_0\rangle$ and the unitary operator $\hat{U}[p,q]$.

This essentially finishes the general description of the approach. The practical scheme is as follows: Suppose that the system initially is in a state $|\Phi(0)\rangle = |\Phi[p(0),q(0)]\rangle$, i.e., the initial values $p(0)$ and $q(0)$ of p and q are known. Then, integrating the equation of motion Eq. (17) for p and q one obtains the values of p and q at time t, i.e., $p(t)$ and $q(t)$. Hence, the state of the system at time t can be determined as

$$|\Phi(t)\rangle = |\Phi[p(t),q(t)]\rangle \quad . \tag{19}$$

In general if the system initially in a state which is not in the basis set G, then we can expand it in terms of the basis set states

$$|\Psi(0)> = \int |\Phi[p_0,q_0]> \frac{dp_0 dq_0}{2\pi\hbar} <\Phi[p_0,q_0]|\psi(0)> \qquad (20)$$

and at later time t we have

$$|\psi(t)> = \int |\Phi[p_0(t),q_0(t)]> \frac{dp_0 dq_0}{2\pi\hbar} <\Phi|[p_0,q_0]|\psi(0)> \qquad , \quad (21)$$

where $|\Phi[p_0(t),q_0(t)]>$ can be evaluated by using the procedure just described above.

The crucial thing we have done during the derivation is the restricted variation. That is, we limited ourselves to considering only the vectors within the basis set G. It implies that we have assumed that if initially the system is in the state $|\Phi(0)> = |\Phi[p(0),q(0)]>$ belonging to the basis set G, then later on the state vector $|\Phi(t)>$ for the system would be within the basis set G all the time and never goes beyond the basis set G. Mathematically it means if

$$|\Phi(0)> = |\Phi[p(0),q(0)]> \in G \text{ for } t = 0$$

then

$$|\Phi(t)> = e^{-itH/\hbar} |\Phi(0)> \simeq \Phi[p(t),q(t)]> \in G \qquad (22)$$

for all t. In general, this is not true. It is only an approximation. The validity of this approximation depends on the choice of the reference vector $|\Phi_0>$ and on the Hamiltonian operator $\hat{H}$. For example, if the Hamiltonian is linear or quadratic in $\hat{P}$ and $\hat{Q}$, it would be exact.

It is straightforward to generalize the above formalism to a system of N degrees of freedom. All that is needed is to replace the scalar label variables with vector label variables

$$q \rightarrow \underset{\sim}{q} \tag{23a}$$

$$p \rightarrow \underset{\sim}{p} \quad , \tag{23b}$$

scalar operators with the vector operators

$$\hat{Q} \rightarrow \hat{\underset{\sim}{Q}} \tag{24a}$$

$$\hat{P} \rightarrow \hat{\underset{\sim}{P}} \quad , \tag{24b}$$

and consequently the scalar product with the vector inner product

$$q\hat{P} \rightarrow \underset{\sim}{q} \cdot \hat{\underset{\sim}{P}} \tag{25a}$$

$$p\hat{Q} \rightarrow \underset{\sim}{p} \cdot \hat{\underset{\sim}{Q}} \tag{25b}$$

Here $\underset{\sim}{q}$ and $\underset{\sim}{p}$ denote the sets of labels $\{q_i\}$ and $\{p_i\}$, i=1,2,...,N, $\hat{\underset{\sim}{Q}}$ and $\hat{\underset{\sim}{P}}$ signify the sets of the operators $\{\hat{Q}_i\}$ and $\{\hat{P}_i\}$, i=1,2,...,N which satisfy the commutation relation

$$[\hat{Q}_i, \hat{P}_i] = i\hbar\delta_{ij}, \quad [\hat{Q}_i, \hat{Q}_j] = 0, \quad [\hat{P}_i, \hat{P}_j] = 0 \quad , \tag{26}$$

where δ_{ij} is the Kronecker delta function.

III. Application to the Collinear Inelastic Scattering of A + BC.

To illustrate the application of the general results obtained above, it is useful to consider the simplest nontrivial example of a collision system that possesses an internal degree of freedom in addition to translation. The Hamiltonian of the system is

$$\hat{H}(\hat{P},\hat{R},\hat{p},\hat{r}) = \hat{H}_0(\hat{P},\hat{R},\hat{p},\hat{r}) + \hat{V}(\hat{r},\hat{R})$$

$$= \frac{\hat{p}^2}{2\mu} + \frac{\hat{p}^2}{2m} + v(\hat{r}) + V(\hat{r},\hat{R}) \tag{27a}$$

with

$$\hat{H}_0(\hat{P},\hat{R},\hat{p},\hat{r}) = \frac{\hat{p}^2}{2\mu} + \frac{\hat{p}^2}{2m} + v(\hat{r}) \quad , \tag{27b}$$

where $\hat{R}$ and $\hat{P}$ are the Cartesian coordinate and momentum for translation of A relative to the center of mass of BC, and $\hat{r}$ and $\hat{p}$ are the Cartesian variables for the vibration of BC.

One must first choose the reference vector. It is obvious that one should take the initial state as the reference state if it is possible, since it corresponds to the zero initial value of label variables and there would be no ambiguity in deciding the initial condition. However, as a reference state it must be a proper vector, and things will be much easier if the expectation values of $\hat{P}$ and $\hat{Q}$ are zero as required by Eq. (9). In the present case, the initial vibrational state corresponds to a proper vector in Hilbert space and can be chosen as a reference vector for the vibrational motion. However, in general it does not fulfill the conditions of Eq. (9)

$$\langle n_i | \hat{p} | n_i \rangle = \bar{p} \neq 0 \qquad (28a)$$

$$\langle n_i | \hat{r} | n_i \rangle = \bar{r} \neq 0 \quad . \qquad (28b)$$

But if the new pair of self-adjoint operators $\hat{p}'$ and $\hat{r}'$

$$\hat{p}' = \hat{p} - \bar{p} \ , \ \hat{r}' = \hat{r} - \bar{r} \qquad (29)$$

are used as the generator of unitary mapping, one will have

$$[\hat{r}', \hat{p}'] = i\hbar \qquad (29')$$

and

$$\langle n_i | \hat{p}' | n_i \rangle = 0 \qquad (30)$$

$$\langle n_i | \hat{r}' | n_i \rangle = 0 \quad . \qquad (30')$$

In contrast, the initial momemtum eigenstate for translation is not a localized state, i.e., is not a proper vector, so it cannot be chosen as a reference vector. Instead a Gaussian wave packet state $|\Phi_{ot}\rangle$ is chosen, which has the representation in position representation,

$$\langle R | \Phi_{ot} \rangle = \frac{1}{(\pi\xi)^{1/4}} \exp(- \frac{R^2}{2\xi^2}) \qquad (31a)$$

and in momentum representation

$$\langle P|\Phi_{ot}\rangle = \sqrt{\frac{\xi}{\hbar}} \ \frac{1}{(\pi)^{1/4}} \ \exp(-\frac{\xi^2}{2\hbar^2}\,P^2) \quad , \quad (31b)$$

where subscript t refers to translational motion, and ξ is a parameter characterizing the width of the wave packet. $|\Phi_{ot}\rangle$ satisfys the condition of Eq. (9)

$$\langle\Phi_{ot}|\hat{P}|\Phi_{ot}\rangle = 0 \qquad\qquad (32a)$$

and

$$\langle\Phi_{ot}|\hat{R}|\Phi_{ot}\rangle = 0 \qquad . \qquad (32b)$$

The direct product of these two reference vectors constitutes the reference vector for the complete system

$$|\Phi_0\rangle = |n_i\rangle|\Phi_{ot}\rangle \qquad . \qquad (33)$$

The unitary mapping operator is then defined by

$$\hat{U}(p_R,q_R,p_r,q_r) = e^{-iq_R\hat{P}/\hbar}\, e^{-iq_r\hat{p}'/\hbar}\, e^{ip_R\hat{R}/\hbar}\, e^{ip_r\hat{r}'/\hbar} \quad , \quad (34)$$

where p_R,q_R,p_r and q_r are label variables, and the unit vector given by

$$|\Phi[p_R(t),q_R(t),p_r(t),q_r(t)]> = \hat{U}[p_R(t),q_R(t),p_r(t),q_r(t)]|\Phi_0>$$

$$= e^{-iq_R(t)\hat{P}/\hbar} \, e^{-iq_r(t)\hat{p}'/\hbar} \, e^{ip_R(t)\hat{R}/\hbar} \, e^{ip_r(t)\hat{r}'/\hbar} \, |n_i>|\Phi_{ot}>$$

$$= e^{-iq_R(t)\hat{P}/\hbar} \, e^{ip_R(t)\hat{R}/\hbar} \, |\Phi_{ot}> \, e^{-iq_r(t)\hat{P}'/\hbar} \, e^{ip_r(t)\hat{r}'/\hbar} \, |n_i>$$

$$= |\Phi_t[p_R(t),q_R(t)]> \, |\Phi_v[p_r(t),q_r(t)]> \quad , \quad (35)$$

where

$$|\Phi_t[p_R(t),q_r(t)]> \equiv e^{-iq_R(t)\hat{P}/\hbar} \, e^{ip_R(t)\hat{R}/\hbar} \, |\Phi_{ot}> \quad (36a)$$

and

$$|\Phi_v[p_r(t),q_r(t)]> \equiv e^{-iq_r(t)\hat{p}'/\hbar} \, e^{ip_r(t)\hat{r}'/\hbar} \, |n_i> \quad (36b)$$

If at t=0 one has

$$|\Phi[p_R(0),q_R(0),p_r(0),q_r(0)]> = |\Phi_t[p_R(0),q_R(0)> \, |n_i>, \quad (37)$$

then, from Eq. (35) and Eq. (36), it is clear that

$$p_r(0) = 0 \quad \text{and} \quad q_r(0) = 0 \quad , \quad (38)$$

or

$$|\Phi_v[p_r(0),q_r(0)]> = |\Phi_v[0,0]> = |n_i> \quad (39)$$

and

$$|\Phi_t[p_R(0),q_R(0)]> = e^{-iq_R(0)\hat{P}/\hbar}\, e^{ip_R(0)\hat{R}/\hbar}\, |\Phi_{ot}> \quad . \quad (40)$$

According to Eq. (18), with help of Eq. (35), it follows that

$$H(p_R,p_r,q_R,q_r) \equiv <\Phi[p_R,p_r,q_R,q_r]|\hat{H}(\hat{P},\hat{R},\hat{p},\hat{r})|\Phi[p_R,p_r,q_R,q_r]>$$

$$= <\Phi[p_R,p_r,q_R,q_r]|\hat{H}'(\hat{P},\hat{R},\hat{p}',\hat{r}')|\Phi[p_R,p_r,q_R,q_r]>$$

$$= <\Phi_o|\hat{H}'(\hat{P}+p_R,\hat{R}+q_R,\hat{p}'+P_r,\hat{r}'+q_r)|\Phi_o>$$

$$= \frac{p_R^2}{2\mu} + \frac{(p_r+\bar{p})^2}{2m} + \bar{v}(q_r,\bar{r}) + \bar{V}(q_R,q_r,\bar{r}) + 0_P \quad (41)$$

where

$$0_P = <n_i|\frac{(\hat{p}')^2}{2m}|n_i> + <\Phi_{ot}|\frac{\hat{P}^2}{2\mu}|\Phi_{ot}>$$

$$= <n_i|\frac{\hat{p}^2}{2m}|n_i> - \frac{\bar{p}^2}{2m} + <\Phi_{ot}|\frac{\hat{P}^2}{2}|\Phi_{ot}> = const., \quad (42)$$

and

$$\bar{v}(q_r,\bar{r}) = <n_i|v(\hat{r}+q_r)|n_i> \quad (43a)$$

$$\bar{V}(q_r,\bar{r},q_R) = <\Phi_{ot}n_i|V(\hat{R}+q_R,\hat{r}+q_r)|\Phi_{ot}n_i> \quad . \quad (43b)$$

Similarly one has

$$H_0(p_R, p_r, q_R, q_r) \equiv \langle\Phi[p_R, p_r, q_R, q_r]|\hat{H}_0(\hat{P}, \hat{R}, \hat{p}, \hat{r})|\Phi[p_R, p_r, q_R, q_r]\rangle$$

$$= \frac{p_R^2}{2\mu} + \frac{(p_r + \bar{P})^2}{2m} + \bar{v}(q_r, \bar{r}) + 0_p \quad . \quad (44)$$

From the scattering theory[6] it is well known that

$$|out\rangle = \hat{S}|in\rangle$$

$$= \lim_{\substack{t_1 \to -\infty \\ t_2 \to +\infty}} e^{i\hat{H}_0 t_2/\hbar} e^{-i\hat{H}t_2/\hbar} e^{i\hat{H}t_1/\hbar} e^{-i\hat{H}_0 t_1/\hbar} |in\rangle \quad (45)$$

where $|out\rangle$ and $|in\rangle$ are out-asymptote and in-asymptote, respectively, and $\hat{S}$ is the scattering operator. Mathematically, as expressed in Eq. (45), t_1 should tend to $-\infty$ and t_2 tends to $+\infty$. But in practice it is sufficient that $|t_1| = |t_{1f}|$ and $t_2 = t_{2f}$ be large enough so that one has

$$e^{-i\hat{H}t/\hbar}|\Phi\rangle \simeq e^{-i\hat{H}_0 t/\hbar}|in\rangle \text{ for } t < t_1 = -|t_{1f}| \quad (46a)$$

and

$$e^{-i\hat{H}t/\hbar}|\Phi\rangle \simeq e^{-i\hat{H}_0 t/\hbar}|out\rangle \text{ for } t > t_2 = t_{2f} \quad . \quad (46b)$$

With this understanding one can rewrite the Eq. (45) as

$$|out> = \hat{S}|in> = \Omega(t_f)|in>$$

$$= e^{i\hat{H}_0 t_{2f}/\hbar} \, e^{-i\hat{H}t_{2f}/\hbar} \, e^{i\hat{H}t_{1f}/\hbar} \, e^{-i\hat{H}_0 t_{1f}/\hbar} \, in$$

$$= \Omega_{(3)} \, \Omega_{(2)} \, \Omega_{(1)} \, |in> \tag{47}$$

with

$$\Omega_{(1)} = e^{-i(-\hat{H}_0)|t_{1f}|/\hbar} \tag{48a}$$

$$\Omega_{(2)} = e^{-i\hat{H}(t_{2f}+|t_{1f}|)/\hbar} \tag{48b}$$

$$\Omega_{(3)} = e^{-i(-\hat{H}_0)t_{2f}/\hbar} \, . \tag{48c}$$

This form suggests that the out-asymptote $|out>$ is obtained from the in-asymptote by following its evolution during 3 separate time periods: in period 1 from $t=0$ to $t=t_{1f}$ the evolution of state is generated by the Hamiltonian $\hat{H}_0$ or $(-\hat{H}_0)$ generates the evolution from $t=0$ to $t=|t_{1f}|$; in period (2) the state is evolved from t_{1f} to t_{2f} according to Hamiltonian $\hat{H}$; and finally in period (3) the state is evolved from $t=t_{2f}$ back to $t=0$ by $\hat{H}_0$.

If one now identifies $|in> = |n_i> \, |\Phi_{ot}[p_R(0),q_R(0)]>$, then by virtue of our approximation Eq. (22) one has

$$|out> = |\Phi[p_R(t_f), p_r(t_f), q_R(t_f), q_r(t_f)]>$$

$$= |\Phi_v(p_r(t_f), q_r(t_f)]> |\Phi_t[p_R(t_f), q_R(t_f)]>$$

$$= e^{-iq_R(t_f)\hat{P}/\hbar}\, e^{-iq_r(t_f)\hat{p}'/\hbar}\, e^{ip_R(t_f)\hat{R}/\hbar}\, e^{ip_r(t_f)\hat{r}'/\hbar}\, |n_i>|\Phi_{ot}>$$

(49)

where $p_R(t_f)$, $q_R(t_f)$, $p_r(t_f)$ and $q_r(t_f)$ are correspondingly determined by classical trajectory calculation as follows: one first integrates the equations of motion Eq. (50) corresponding to $H_0(p_R, p_r, q_R, q_r)$ from $t=0$ to $t=t_{1f}$

$$\frac{dq_R(t)}{dt} = \frac{p_R(t)}{\mu} \tag{50a}$$

$$\frac{dq_r(t)}{dt} = \frac{p_r + \bar{p}}{m} \tag{50b}$$

$$\frac{dp_R(t)}{dt} = 0 \tag{50c}$$

$$\frac{dp_r(t)}{dt} = -\frac{\partial \bar{v}(q_r, \bar{r})}{\partial q_r} \tag{50d}$$

with initial conditions

$$q_R = q_R(0),\ p_R = p_R(0),\ q_r = 0,\ p_r = 0 \text{ at } t=0 \quad , \tag{51}$$

then continuously integrates Eq. (52) corresponding to $H(p_R, p_r, q_R, q_r)$

from $t = t_{1f}$ to $t = t_{2f}$

$$\frac{dq_R(t)}{dt} = \frac{p_R(t)}{\mu} \tag{52a}$$

$$\frac{dq_r(t)}{dt} = \frac{p_r + \bar{P}}{m} \tag{52b}$$

$$\frac{dP_R(r)}{dt} = \frac{-\bar{V}(\bar{r}, q_r, q_R)}{\partial q_R} \tag{52c}$$

$$\frac{dP_r(t)}{dt} = \frac{-\partial \bar{v}(q_r, \bar{r})}{\partial q_r} - \frac{\partial \bar{V}(q_r, \bar{r}, q_R)}{\partial q_r} \tag{52d}$$

and finally integrates Eq. (50) from $t = t_2$ back to $t = 0$.

The projection of $|out\rangle$ on the final state $|n_t P^f\rangle$ then can be readily calculated

$$\langle n_f P^f | out \rangle = \langle n_f | \Phi_v[p_r(t_f), q_r(t_f)] \rangle \langle P^f | \Phi_t[P_R(t_f), q_R(t_f)] \rangle \ , \tag{53}$$

where

$$\langle P^f | \Phi_t[P_R(t_f), q_R(t_f)] \rangle$$

$$= \langle p^f | e^{-iq_R(t_f)\hat{P}/\hbar} \ e^{ip_R(t_f)\hat{R}/\hbar} | \Phi_{ot} \rangle$$

$$= \sqrt{\frac{\xi}{\hbar}} \ \frac{1}{(\pi)^{1/4}} \ \exp[-\frac{i}{\hbar} q_R(t_f) \ P^f - \frac{\xi^2}{2\hbar^2}(P^f - p_R(t))^2] \quad .$$

$$\tag{54}$$

and

$$\langle n_f | \Phi_v [p_r(t_f), q_r(t_f)] \rangle$$

$$= \langle n_f | e^{-iq_r(t_f)\hat{p}'/\hbar} \, e^{ip_r(t_f)\hat{r}'/\hbar} | n_i \rangle$$

$$= \langle n_f | e^{iq_r(t_f)\bar{p}/\hbar} \, e^{-ip_r(t_f)\bar{r}/\hbar} \, e^{-iq_r(t_f)\hat{p}/\hbar} \, e^{ip_r(t_f)\hat{r}/\hbar} | n_i \rangle$$

$$= e^{iq_r(t_f)\bar{p}/\hbar} \, e^{-ip_r(t_f)\bar{r}/\hbar} \int_{-\infty}^{\infty} dr \, \langle n_f | r \rangle \, e^{ip_r(t_f)[r - q_r(t_f)]/\hbar}$$

$$\langle r - q_r(t_f) | n_i \rangle \qquad . \quad (55)$$

Here $|n_f\rangle$ and $|P^f\rangle$ are final vibrational state and translational momentum eigenstate, respectively.

On the other hand, one has

$$\langle n_f P^f | \text{out} \rangle = \langle n_f P^f | \hat{S} | \text{in} \rangle$$

$$= \langle n_f P^f | \hat{S} | n_i \rangle | \Phi_t (p_R(0), q_R(0)) \rangle$$

$$= \int \frac{dp}{2\pi\hbar} \, \langle n_f P^f | \hat{S} | n_i P \rangle \langle P | \Phi_t (P_R(0), q_R(0)) \rangle$$

$$= S_{n_f \leftarrow n_i}(E) \int \frac{\mu}{2\pi\hbar P} \, dE \, \delta(E - E_0)$$

$$\times \frac{2\pi\hbar}{\mu} \sqrt{PP^f} \langle P | \phi_t [p_R(0), q_R(0)] \rangle$$

$$= \sqrt{\frac{P^f}{P^i}} \, \langle P^i | \Phi_t [p_R(0), q_R(0)] \rangle \, S_{n_f \leftarrow n_i}(E) \qquad .$$

or

$$S_{n_f \, n_i}(E) = \sqrt{\frac{p^i}{p^f}} \; \frac{\langle n_t p^f | out \rangle}{\langle p^i | \phi_t [p_R(0), q_R(0)] \rangle} \tag{56}$$

with

$$p^i = \sqrt{2\mu(E_0 - \varepsilon_{n_i})} \quad , \quad p^f = \sqrt{2\mu(E_0 - \varepsilon_{n_i})} \quad , \tag{57}$$

and

$$\langle p^i | \phi_t [p_R(0), q_R(0)] = \sqrt{\frac{\xi}{\pi}} \; \frac{1}{(\pi)^{1/4}} \; \exp[(-\frac{i}{\hbar} q_R(0) p^i) - \frac{\xi^2}{2\hbar^2} (p^i - p_R(0))^2] \tag{58}$$

Here ε_n is the vibrational energy of molecule BC in the state n and E_0 is the total energy of the whole system. Eq. (56) is exact. Now if an approximation Eq. (53) is used, then by virtue of Eq. (54) and Eq. (55) it is obtained that

$$S_{n_f \leftarrow n_i}(E) = \sqrt{\frac{p^i}{p^f}} \; \frac{\langle p^f | \phi_f [p_R(t), q_R(t)] \rangle}{\langle p^i | \phi_f [p_R(0), q_R(0)] \rangle} \langle n_f | \phi_v [p_r(t_f), q_r(t_f)] \rangle$$

$$= \sqrt{\frac{p^i}{p^f}} \; e^{-i/\hbar \, \gamma(t_f)} \; e^{-\frac{\xi^2}{2\hbar^2} B(t_f)} \int_{-\infty}^{\infty} dr \, \langle n_f | r \rangle e^{ip_r(t_f)[r-q_r(t_f)]/\hbar}$$

$$\langle r - q_r(t_f) | n_i \rangle \quad , \tag{59}$$

where

$$\gamma(t_f) = q_R(t_f)P^f - q_R(0)P^i + p_r(t_f)\bar{r} - q_r(t_f)\bar{p} \tag{60a}$$

$$B(t_f) = [P^f - p_R(t_f)]^2 - (P^i - p_R(0))^2 \quad . \tag{60b}$$

Thus, the transition probability can be calculated,

$$P_{n_f \leftarrow n_i} = |S_{n_f \leftarrow n_i}(E)|^2 = \frac{P^i}{P^f} \, e^{-\frac{\xi^2}{\hbar^2} B(t_f)}$$

$$\times \left| \int_{-\infty}^{\infty} dr \, \langle n_f | r \rangle e^{ip_r(t_f)[r - q_r(t_f)]/\hbar} \langle r - q_r(t_f) | n_i \rangle \right|^2 \quad . \tag{61}$$

where $p_R(t_f)$, $q_R(t_f)$, $p_r(t_f)$ and $q_r(t_f)$ are determined by calculating one classical trajectory.

IV. Example: The Vibrationally Inelastic Scattering of Collinear
     He + H$_2$.

To test the potential usefulness of this new approach a

calculation for the Secrest-Johnson model[7] of collinear He + H$_2$

vibrationally inelastic scattering has been carried out. In the

usual dimensionless coordinate system the Hamiltonian reads

$$\hat{H}(\hat{P},\hat{R},\hat{p},\hat{r}) = \frac{\hat{P}^2}{2\mu} + \frac{\hat{p}^2}{2} + \frac{\hat{r}^2}{2} + \exp(\alpha(\hat{r}-\hat{R})) \tag{62}$$

with

$$\mu = \frac{2}{3} \text{ and } \alpha = 0.3.$$

In this case the vibration states $|n\rangle$ are the eigenstates of

harmonic oscillator, so that

$$\langle n_i|\hat{p}|n_i\rangle = \bar{p} = 0 \tag{63}$$

$$\langle n_i|\hat{r}|n_i\rangle = \bar{r} = 0 \quad . \tag{64}$$

Also, the "classical" Hamiltonians have the form:

$$H_0 = \frac{P_R^2}{2} + \frac{P_r^2}{2} + \frac{q_r^2}{2} + 0_p + 0_v \tag{65}$$

with

$$0_p = \langle n_i|\frac{\hat{p}^2}{2}|n_i\rangle + \langle \phi_{ot}|\frac{\hat{p}^2}{2}|\phi_{ot}\rangle = \text{const.} \tag{66}$$

and

$$O_v = <n_i|\frac{\hat{r}^2}{2}|n_i> = \text{const.} \qquad , \qquad (67)$$

and

$$H = H_0 + A \exp \alpha \ (q_r - q_R) \qquad (68)$$

with

$$A = <n_i|e^{\alpha\hat{r}}|n_i><\Phi_{ot}|e^{-\alpha\hat{R}}|\Phi_{ot}> = \text{const.} \qquad . \qquad (69)$$

It immediately follows that the equations of motion for label variables are:

for H_0

$$\frac{dq_R}{dt} = \frac{p_R}{\mu} \qquad , \qquad \frac{dq_r}{dt} = p_r \qquad ,$$

$$\frac{dp_R}{dt} = 0 \qquad , \qquad \frac{dp_r}{dt} = -q_r \qquad , \qquad (70)$$

and for H

$$\frac{dq_R}{dt} = \frac{p_R}{\mu} \quad , \quad \frac{dq_r}{dt} = p_r$$

$$\frac{dp_R}{dt} = A \, \alpha \, \exp \alpha \, (q_r - q_R)$$

$$\frac{dp_r}{dt} = -q_r - A \, \alpha \, \exp \alpha \, (q_r - q_R) \quad . \tag{71}$$

In this example the matrix element Eq. (55) has a simple analytic expression. In order to see this let us first make the following transformations:

$$\hat{a} \equiv (\hat{r} + i\hat{p})/\sqrt{2} \quad , \quad \hat{a}^\dagger \equiv (\hat{r} - i\hat{p})/\sqrt{2} \tag{72}$$

$$Z(t) \equiv (q_r(t) + ip(t))/\sqrt{2} \quad , \quad \text{and} \quad \theta(t) \equiv \tan^{-1} \frac{p_r(t)}{q_r(t)} \quad . \tag{73}$$

It then follows that (for the details, see the Appendix)

$$\langle n_f | e^{-iq_r(t_f)\hat{p}} \, e^{ip_r(t_f)\hat{r}} | n_i \rangle$$

$$= e^{-i\frac{1}{2}|z(t_f)|^2 \sin 2\theta(t_f)} \, e^{-\frac{1}{2}|z(t_f)|^2}$$

$$\times \langle n_f | e^{\hat{a}^\dagger z(t_f)} \, e^{-z^*(t_f)\hat{a}} | n_i$$

$$= e^{-i\frac{1}{2}|z(t_f)|^2 \sin 2\theta(t_f)} \, e^{-\frac{|z(t_f)|^2}{2}} \, e^{i(n_f - n_i)\theta(t_f)}$$

$$\times \sum_{k=0}^{n_i} (-1)^k \frac{\sqrt{n_i! n_f!} |z(t_f)|^{n_f - n_i + 2k}}{k!(n_i - k)!(n_f - n_i + k)!} \quad , \tag{74}$$

where $z^*(t_f) = [q_r(t_f) - p_r(t_f)]/\sqrt{2}$ and $|z| = \sqrt{z \cdot z^*}$. By virtue of Eq. (74), the transition probability Eq. (61) becomes

$$P_{n_f \leftarrow n_i} = \frac{p^i}{p^f} \exp\{-\frac{\xi^2}{2}[(P^f - p_R(t_f))^2 - (P^i - p_R(0))^2]\}\exp\left|-|z(t_f)|^2\right|$$

$$\times \left| \sum_{k=0}^{n_i} (-1)^k \frac{\sqrt{n_i! \, n_f!}}{k!(n_i-k)!(n_f-n_i+k)!} |z(t_f)|^{n_f-n_i+2k} \right|^2 ,$$

$$(75)$$

If this theory gave $|out\rangle = \hat{S}|in\rangle = \hat{S}|n_i\rangle|\Phi_{ot}[p_R(0),q_R(0)]\rangle$ exactly, the transition amplitude $S_{n_f \leftarrow n_i}(E)$ obtained by using Eq. (56) would be independent of the choice of $P_R(0)$ and $q_R(0)$. Since it is an approximation, though, the results of a calculation do depend on the choice of $p_R(0)$. Since $p_R(0)$ is the average value of the momentum $\hat{p}$ in the initial wave packet state $|\Phi_f[p_R(0),q_R(0)]\rangle$ with initial and final vibrational states $|n_i\rangle$ and $|n_f\rangle$ and total energy E_0 specified, physical intuition suggests that the usual semiclassical choice of $p_R(0)$ should be reasonable

$$p_R(0) = \sqrt{2\mu(E_0 - \bar{\varepsilon}_n)} = \sqrt{2\mu(E_0 - \frac{\varepsilon_{n_i} + \varepsilon_{n_f}}{2})} \quad . \qquad (76)$$

The choice of $q_k(0)$ is more and less arbitrary, it only affects the determination of t_{1f} and t_{2f} and so long as the conditions Eq. (46) are satisfied, $q_R(0)$ can be any value. Furthermore, from Eq. (70) and Eq. (71) one can see that the parameter ξ do not have any dynamic effect on the $p_R(t)$ and $|z(t)|$, but the probability $P_{n_f \leftarrow n_i}$ does depend

on ξ as seen in Eq. (75). In order to eliminate this ξ dependence and to symmetrilize the transition probability we choose ξ such that

$$\frac{p^i_f}{p^f} e^{-\frac{\xi^2}{\hbar} [(P^f - p_R(t_f))^2 - (P^i - p_R(0))^2]\}} = 1 \quad .$$

Then, the symmetrilized transition probability $P_{n_f \leftarrow n_i}$ has the simple expression

$$P_{n_f \leftarrow n_i} = e^{-|z(t_f)|^2} \left| \sum_{k=0}^{n_i} (-1)^k \frac{\sqrt{n_i! n_f!}}{k!(n_i-k)!(n_f-n_i+k)!} |z(t_f)|^{n_f-n_i+2k} \right|^2 \quad .$$

$$(77)$$

The results from Eq. (77) are given in Table I where for comparison the exact quantum mechanical results of reference 7 are also included. In Figure 1 we pictorially present the results for total energy $E_0 = 4,6$, and 10 in unit of $\hbar\omega$. For a given total energy E_0 and an initial vibrational state n_i only one "classical" trajectory is needed to be calculated to determine the transition probability to a final vibrational state n_f.

The comparison in Table 1 and Figure 1 shows that the present approach describes the inelastic scattering process encouragingly well. One obtains reasonably good results over a wide range of energies for a great variety of Δn transitions.

V.   Discussion

The principal idea of the present semiclassical approach has been to use classical mechanics in a formal sense to determine the time evolution of the state vector. In the present application one recognizes many similarities to time-dependent wave packet methods, but there are significant differences.

The wave packet methods[2] are essentially a combination of time-dependent Hartree-Fock theory and Ehrenfest's theorem; and an important aspect of them are the classical parameters, i.e., the coordinates and momenta of the particles. The actual equations of motion that characterize the wave packet, however, are non-classical. In contrast, the present approach stems from the restricted variation of the action functional. This leads to a set of classical Hamilton's equations of motion for the label variables, which may or may not have a direct physical interpretation; the effective Hamiltonian, however, is not necessarily identical to the classical Hamiltonian.

Also, as seen with the example treated above, the present approach deals equally well with translational wavefunctions (as a gaussian wave packet) and with stationary states. Thus one can easily use initially excited vibrational states, whereas the usual wave packet methods must represent excited states as linear combinations of gaussians. It is also clear that the present approach can deal equally well with quantum systems that have no classical analog, e.g., spin systems.[3] It appears also that it will be easier to deal with rotational degrees of freedom, so that the present method may be more easily generalized to deal with three-dimensional collision systems than wave packet approaches.

Finally, the present approach has encouraging practical features; e.g., only one classical trajectory is necessary to generate the probability for a given transition. In any event, however, the method is an approximation, the accuracy of which will depend on the nature of the system investigated and the choice of the reference vector. It is sufficiently promising, though, that its generalization to 3-d systems and also to polyatomic dynamics seems worthwhile.

Acknowledgments

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Table 1. Transition Probability for Collinear He + H_2 Vibrationally Inelastic Scattering.

n_i	n_f	$E_{tol}(\hbar\omega)$ 10		8		6		4		3	
		QM	our	QM	our	QM	our	QM	our	QM	our
0	0	0.060	0.0866	0.204	0.2284	0.538	0.4976	0.891	0.8282	0.979	0.9437
	1	0.218	0.2452	0.434	0.3473	0.394	0.31522	0.108	0.1005	0.0221	0.0230
	2	0.366	0.2704	0.291	0.1945	0.064	0.05454	0.00122	0.00158		
	3	0.267	0.15003	0.071	0.04606						
	4	0.089	0.04525								
1	0	0.218	0.24516	0.434	0.3573	0.394	0.3152	0.108	0.1005	0.0221	0.02302
	1	0.286	0.1272	0.034	0.0012	0.244	0.23688	0.8502	0.8376	0.9781	0.98124
	2	0.009	0.01359	0.220	0.232	0.345	0.31564	0.0418	0.04495	0.0008	
	3	0.170	0.1926	0.261	0.2141	0.037	0.03879				
	4	0.240	0.1776	0.051	0.04614						
	5	0.071	0.05645								
2	0	0.366	0.27044	0.291	0.19446	0.068	0.0545	0.00122	0.00158		
	1	0.009	0.01359	0.220	0.2324	0.345	0.3156	0.0418	0.04495		
	2	0.207	0.17013	0.034	0.01151	0.347	0.3399	0.9556	0.96887		
	3	0.018	0.0000154	0.250	0.243	0.233	0.23868	0.00133	0.002047		
	4	0.169	0.17517	0.189	0.1812	0.006	0.00878				
	5	0.194	0.16524								
	5	0.034	0.0401								

Appendix

Let $\hat{P}$ and $\hat{Q}$ be a pair of self-adjoint operators which satisfy the canonical commutation relation

$$[\hat{Q},\hat{P}] = i\hbar \quad . \tag{A.1}$$

Introduce a unitary operator

$$\hat{U}[p,q] \equiv e^{-iq\hat{P}/\hbar} \, e^{ip\hat{Q}/\hbar} \tag{A.2}$$

where p and q are the parameters. Now let us do the following transformations:

$$\hat{a} \equiv (\hat{Q} + i\hat{P})/\sqrt{2\hbar} \quad , \quad \hat{a}^{\dagger} \equiv (Q-iP)/\sqrt{2\hbar} \quad , \tag{A.3}$$

$$z = (q + ip)/\sqrt{2\hbar} \quad \text{and} \quad \theta = \tan^{-1}\frac{p}{q} \quad . \tag{A.4}$$

Here the $\hat{a}$ and $\hat{a}^{\dagger}$ are well known annihilation and creation operators. Then it follows that

$$i(-q\hat{P}+p\hat{Q})/\hbar = \hat{a}^{\dagger}z - z^{*}\hat{a} \tag{A.5}$$

$$[\hat{a},\hat{a}^{\dagger}] = 1 \quad , \tag{A.6}$$

$$\hat{a}^{k}|n\rangle = \sqrt{\frac{n!}{(n-k)!}} \, |n-k\rangle \quad , \tag{A.7}$$

$$|n\rangle = \frac{(\hat{a}^{\dagger})^{n}}{\sqrt{n!}} \, |o\rangle \tag{A.8}$$

and

$$-pq = \frac{i\hbar}{2}(z+z^*)(z-z^*)$$

$$= \frac{i\hbar}{2}(z^2-z^{*2}) = -\hbar\,|z|^2\sin2\theta \quad , \qquad (A.9)$$

where n is the eigenstate of harmonic oscillator. Using Eq. (A.5) and Eq. (A.9) gives

$$\langle n_f|e^{-iq\hat{P}/\hbar}\,e^{ip\hat{Q}/\hbar}|n_i\rangle$$

$$= e^{-ipq/2\hbar}\langle n_f|e^{-iq\hat{P}/\hbar+ip\hat{Q}/\hbar}|n_i\rangle$$

$$= e^{-i\frac{|z|^2}{2}\sin2\theta}\langle n_f|e^{\hat{a}^\dagger z-z^*\hat{a}}|n_i\rangle$$

$$= e^{-i\frac{|z|^2}{2}\sin2\theta}\,e^{-\frac{|z|^2}{2}}\langle n_f|e^{\hat{a}^\dagger z}\sum_{k=0}^{\infty}\frac{(-z^*)^k}{k!}\hat{a}^k|n_i\rangle$$

$$(A.10)$$

With help of Eq. (A.7) and (A.8) one has

$$\langle n_f|e^{\hat{a}^\dagger z}\sum_{k=0}^{\infty}\frac{(-z^*)^k}{k!}\hat{a}^k|n_i\rangle$$

$$= \langle n_f|e^{\hat{a}^\dagger z}\sum_{k=0}^{n_i}(-1)^k z^{*k}\frac{\sqrt{n_i!}}{k!\sqrt{(n_i-k)!}}|n_i-k\rangle$$

$$= \sum_{k=0}^{n_i}\langle n_f|e^{\hat{a}^\dagger z}\sqrt{\frac{n_i!}{(n_i-k)!}}(-1)^k z^{*k}\frac{\hat{a}^{\dagger(n_i-k)}}{k!\sqrt{(n_i-k)!}}|0\rangle$$

$$= \sum_{k=0}^{n_i} (-1)^k (z^*)^k \frac{\sqrt{n_i!}}{k!(n_i-k)!} \langle n_f | (\hat{a}^\dagger)^{n_i-k} e^{\hat{a}^\dagger z} | 0 \rangle$$

$$= \sum_{k=0}^{n_i} (-1)^k (z^*)^k \frac{\sqrt{n_i! n_f!}}{k!(n_i-k)!} \frac{1}{\sqrt{(n_f-n_i+k)!}} \langle n_f-n_i+k | z \rangle e^{\frac{|z|^2}{2}}$$

$$= \sum_{k=0}^{n_i} (-1)^k (z^*)^k \frac{\sqrt{n_i! n_f!}}{k!(n_i-k)!(n_f-n_i+k)!} z^{n_f-n_i+k}$$

$$= \sum_{k=0}^{n_i} (-1)^k \frac{\sqrt{n_i! n_f!}}{k!(n_i-k)!(n_f-n_i+k)!} |z|^{n_f-n_i+2k} e^{i(n_f-n_i)\theta} ,$$

$$(A.11)$$

where $|z\rangle \equiv e^{\hat{a}^\dagger z} |0\rangle e^{-\frac{|z|^2}{2}}$ is well known to be a coherent state[8] which is the eigenstate of the operator $\hat{a}$ such that
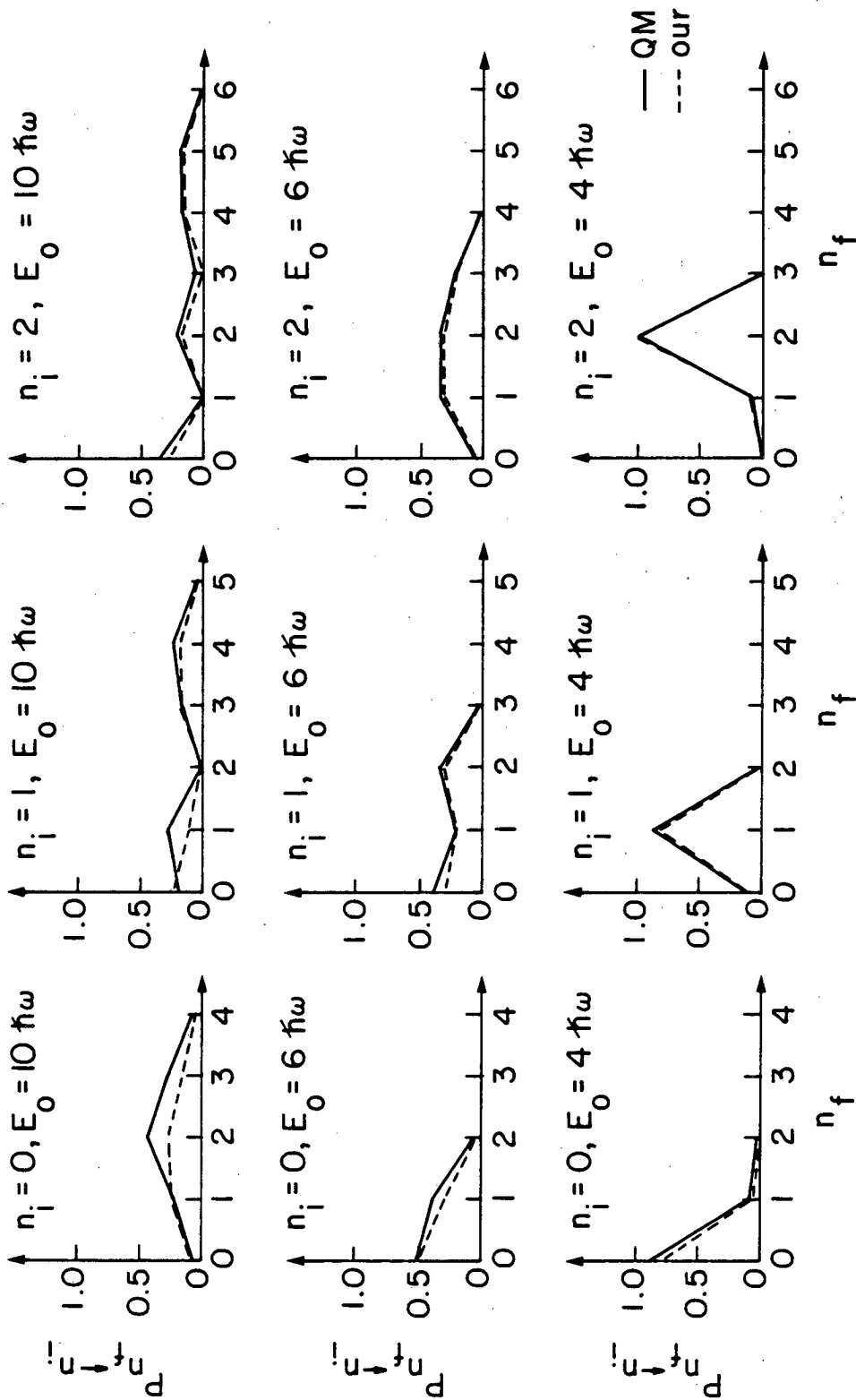
$$\hat{a} |z\rangle = z |z\rangle \qquad (A.12)$$

and

$$\langle n | z \rangle = e^{-\frac{|z|^2}{2}} \frac{z^n}{\sqrt{n!}} . \qquad (A.13)$$

Substituting Eq. (A.11) into Eq. (A.10) yields

$$\langle n_f | e^{-iq\hat{P}/\hbar} e^{ip\hat{Q}/\hbar} | n_i \rangle$$

$$= e^{-i\frac{|z|^2}{2}\sin 2\theta} e^{-i(n_f-n_i)\theta} e^{-\frac{|z|^2}{2}} \sum_{k=0}^{n_i} (-1)^k \frac{\sqrt{n_i! n_f!}}{k!(n_i-k)!(n_f-n_i+k)!}$$

$$|z|^{n_f-n_i+2k} . \qquad (A.14)$$

Figure Captions

1. Transition probability for collinear He + H_2 vibrationally inelastic

   scattering.

Figure 1

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